Study on Preparation of Composite Materials of Montmorillonite

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***Abstract*- Granulated composite materials were prepared by using the mixture of montmorillonite, fly ash and certain amount of cementing agent. The granulated composite materials were used to treat waste water containing Cu^{2+}. The mixture ratio of montmorillonite/fly ash, temperature of calcination and the amount of cementing agent were investigated. The experimental study results showed that the optimum technological conditions of preparing composite materials were as follows: the mixture ratio of montmorillonite and fly ash was 6:4; the calcination temperature was 450°C; the proportion of industrial starch used as an additive was 10%; the diameter of the granular was 1～2mm. Physical tests of granulated adsorption materials showed that the water adsorption capacity was 31.80%, the apparent porosity was 46.82%, the bulk density was 1.47 kg/m^3, the compressive strength was 5.28 MPa, and the surface area was 10.28 m^2 / g. The composite adsorbent materials prepared under the above conditions exhibited high adsorptive performance.**

Keywords-montmorillonite; fly ash; granulation; adsorption

Montmorillonite has been studied with great progress in the application of environmental protection since 1980s. Montmorillonite was used as environmental protection material primarily in wastewater treatment, which could be seen from the present references. Whether montmorillonite as single sodium modified or composite materials, the main purpose is to improve its adsorption capacity to use as adsorbent in wastewater purification. It not only absorbs a mass of organic suspended matter and heavy metal irons, but also removes microorganism such as bacteria, virus and other microorganism. Therefore, the montmorillonite and its products can be used for treating a variety of wastewater. Furthermore, lots of researches indicated that utilizing montmorillonite to treat wastewater contained heavy metal irons showed not only better effect but also much more economical, which explored a feasible way for the exploitation and utilization of montmorillonite.

It was attracted much attention that using montmorillonite mineral, fly ash and other industrial wastes as adsorption materials to remove heavy metal irons in wastewater because of its obvious economic benefits and social significance. Most of the treatment technologies adopted powdery adsorbent to process wastewater，but it was very difficult for the subsequent solid-liquid separation process，because the powdery adsorbent material was very small and easy to disperse when it was mixed with water. It was easy to form new industrial sludge which would have much more harmfulness of secondary pollution due to the concentration of heavy metal irons. Although the treatment effect of powdery adsorbent was fine, it had many problems in practical application. In order to solve the above problems of powdery adsorbent processing wastewater the experiment was made to study the technological conditions of preparing the granulated adsorption materials of montmorillonite and its adsorption performance on Cu^{2+}.

I. EXPERIMENTAL

A. Materials

The raw materials used in the experiments were the calcium montmorillonite from Liaoning province and the fly ash from a coal-fired power plant in Wuhan. The X-ray fluorescence spectrometer quantitative analysis was made by Test Center of Wuhan University of technology. The chemical composition of montmorillonite and fly ash was as Table 1 and Table 2.

TableI CHEMICAL COMPOSITION OF MONTMORILLONITE

Ingredient	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Wt%	56.78	6.56	17.03	0.73	2.76	3.65	0.85	0.39

Ingredient	MnO	H_2O^+	H_2O^-	ignition loss	total
Wt%	0.08	10.29	4.23	10.04	99.46

TableII CHEMICAL COMPOSITION OF FLY ASH

Ingredient	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
Wt%	38.66	20.86	4.25	0.98	18.94	1.21	1.81	0.42
Ingredient	SO_3	P_2O_5	Ignition loss	Total				
Wt%	3.33	0.35	8.64	99.45				

B. Instruments and reagents

The instruments and reagents used in the experiments were shown as Table 3 and Table 4.

TableIII EXPERIMENTAL INSTRUMENT LIST

Equipment	Type	Manufacturer	Use
Air-bath oscillator	HZQ-C	Harbin Donglian Electronic &Technology Development Co., Ltd	Oscillation adsorption
Electric-heated thermostatic air-blowing dryer	DHG－9075A	Shanghai Yiheng Instruments Company	Dry
Resistance furnace temperature controller	KSY-12-16S	Shanghai Experimental Electric Furnace Factory	Roasting
High speed tabletop centrifuge	800	Shanghai Surgical Instrument Factory	Solid-liquid separation
Flame atomic absorption spectrometer	AVANTA M	Australia GBC Company	Ion concentration determination
Specific surface area and aperture tester	2360	American Gemini Company	Specific surface area determination
X-ray diffraction	D/MAX-IIIA Axios	Japan RIGAKU Company	Phase analysis
X-ray fluorescence spectrometer Transmission electron microscopy	H-600STEM/EDX PV9100	The Dutch Panalytical Company Japan HITACHI Company	Quantitative analysis Morphology analysis

TableIV EXPERIMENTAL REAGENT LIST

Drug	Chemical formula	Purity	Manufacturers
Copper sulfate	$CuSO_4{\cdot}5H_2O$	Analytically pure	Tianjin Bodi Chemical Co., Ltd
Sodium acetate anhydrous	$C_2H_3NaO_2$	Analytically pure	Sinopharm Chemical Reagent Co., LtdS
Glacial acetic acid	CH_3COOH	Analytically pure	Tianjin Guangcheng Chemicals Co., Ltd
Sodium ethylene diamine tetraacetate	$C_{31}H_{28}N_2Na_4O_{13}S$	Analytically pure	Tianjin Guangcheng Chemicals Co., Ltd

C. Methods

1) Preparation of Montmorillonite Composite Particle Materials:

The montmorillonite composite particle materials were prepared using appropriate amount of montmorillonite and fly-ash, mixing with a certain proportion of additives, adding appropriate amount of distilled water and standing aging, making by hand to form spheric particles with the diameter of 1～3mm, natural aging for 40min and then drying for 1h under 105℃ , finally roasting at high temperature for 2h.

2) Method for Adsorption Experiments:

A certain quantity of standard Cu^{2+} solution and

amount of montmorillonite composite particles adsorbent were added into volumetric flask, mixing adsorbed in an oscillator, centrifugalized with a high speed tabletop centrifuge. 5mL centrifugal solution, 5mL buffer solution and 5mL 0.1mol/L EDTA were added into a 50mL tube. Then distilled water was added to 50mL scale line and shaken well. The absorbency of solution was determined by a grating spectrophotometer of 7200 type under the wavelength of 733nm and compared with that there was not added Cu^{2+} solution. The concentration of Cu^{2+} solution was calculated. The adsorption efficiency of Cu^{2+} on montmorillonite/fly ash composite materials was calculated according to the concentration changes before and after adsorption.

Adsorption ratio was calculated as follow formula:

$\eta=(Co-C)\times100\%/Co$

η: adsorption ratio of Cu^{2+} on composite particles adsorbent (%)

Co: concentration of Cu^{2+}before adsorption (mg/L)

C: concentration of Cu^{2+}after adsorption (mg/L)

3) Determination of Granular Spallation Lost Ratio:

A certain amount of particles were taken into conical flask with 100mL distilled water and oscillated in a stable temperature horizontal shaking bath with the frequency of 110r/min for a while at a certain temperature. Then the powder produced by crushing adsorption material was washed by deionized water and rest wet granules were dried up to constant weight in the drying oven. The quality of remaining intact granules was weighed after cooling down to room temperature.

Granular spallation lost ratio was calculated as the following formula:

$q=(Mo-M)\times100\%/Mo$

q: granular spallation lost ratio(%)

Mo: quality of granules before adsorption (g)

M: quality of remaining intact granules after adsorption (g)

II. STUDY ON THE PREPARATION TECHNOLOGY OF GRANULATED COMPOSITE ADSORPTION MATERIALS OF MONTMORILLONITE

The results of preparation technology research of granular adsorbent showed that adsorption ratio and spallation lost ratio of granules were influenced by several factors, which were calcination temperature, ash rate, proportion of additive, particle size of adsorbent and calcinations time. The purpose of this experiment was to prepare adsorption materials with both high adsorption ability and suitable strength, but it seems always contradictive. Therefore, the two factors would be comprehensively considered in this experiment in order to determine the optimum technological conditions.

A. Effect of Calcination Temperature

A certain quantity of montmorillonite and fly ash were weighed and mixed by the ratio of 5:5, and some additives were added into the mixture. Montmorillonite/ fly ash composite particles were prepared as above technology. They were roasted for 2h under different temperature conditions in muffle furnace, and cooled down to the room-temperature. The composite particles were used to process simulated wastewater contained Cu^{2+}. Adsorption experimental conditions were as follows: the initial concentration was 200 mg/L; the adsorbent of granules was 12g/L; the adsorption reaction time was 60min. Experimental results were shown in Fig.1.

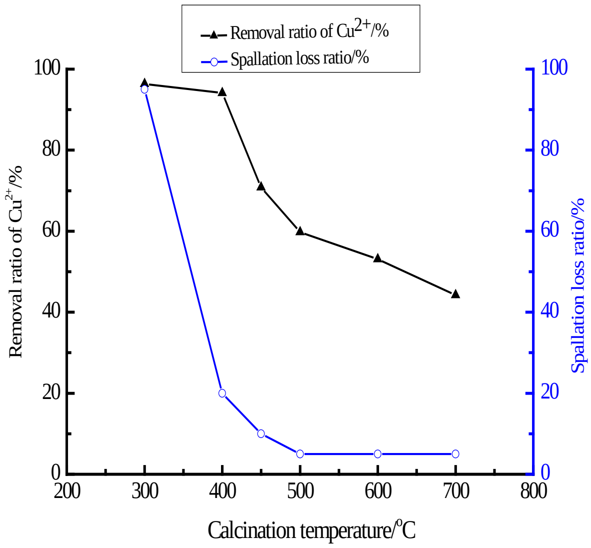

Fig.1 Effect of calcination temperature on removal efficiency

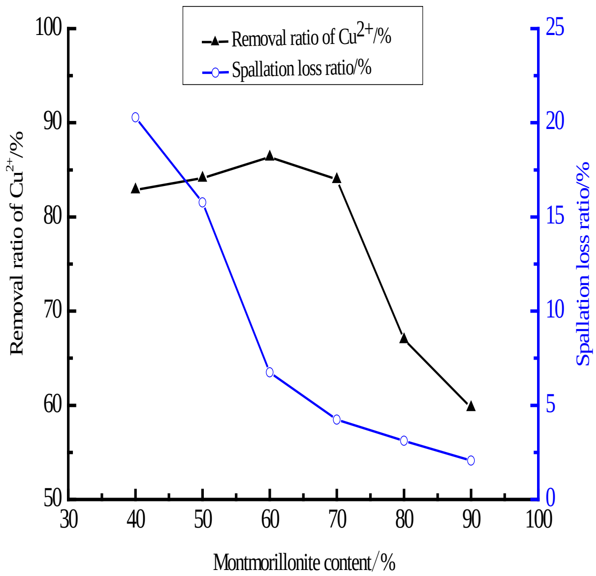

Fig.2 Effect of mixing ratio of montmorillonite and fly ash on removal efficiency

Fig.1 showed that both the curves of removal rate of adsorption and lost ratio were downtrend with the increase of calcination temperature. When the temperature was 300℃, there was the highest adsorption rate of 96.34％ and spallation lost ratio of 95％. When the temperature was 700℃, adsorption rate and lost ratios was 5％and 44.23％respectively. Therefore, high temperature calcination was in favor of increasing particle strength, but it decreased the adsorption

rate correspondingly. High strength and high adsorption rate could not be given consideration simultaneously. When the temperature was 450℃, adsorption rate was 70.84% and lost ratio was10％. Calcination temperature was determined as 450℃ after comprehensively considering, so the calcination temperature of subsequent experiments was fixed at 450℃.

B. Effect of Mixing Ratio of Montmorillonite/Fly Ash

A certain quantity of montmorillonite was weighed and mixed with fly ash by different mass ratios. Composite particles of montmorillonite/ fly ash were prepared and the calcination temperature was 450℃. An adsorption experiment was made after the granules cooled down to room-temperature under the same conditions of 2.1. Experimental results were shown in Fig.2.

Fig.2 showed that removal rate of adsorption was downtrend while spallation loss ratio decreases sharply with the increase of content of montmorillonite. When montmorillonite content was 40-60％, adsorption rate of granular adsorbent was higher as well as spallation loss ratio. When montmorillonite content was more than 60％, loss ratio had not changed much more but adsorption rate decreases sharply. Thus, montmorillonite content was determined on 60％: The best mixture ratio of montmorillonite and fly ash was 6:4. So mixture ratio of montmorillonite and fly ash of subsequent experiment was fixed on 6:4.

C. Effect of Additive Ratio

A certain quantity of montmorillonite and fly ash were weighed and mixed by the ratio of 6:4. Industrial starch was added with different mass ratios. Composite particles of montmorillonite/ fly ash were prepared by the technology of 1.3.1 and calcination temperature was 450℃. Adsorption experiment was carried after the granules cooled down to room-temperature under the same conditions of 2.1. Experimental results were shown in Fig.3.

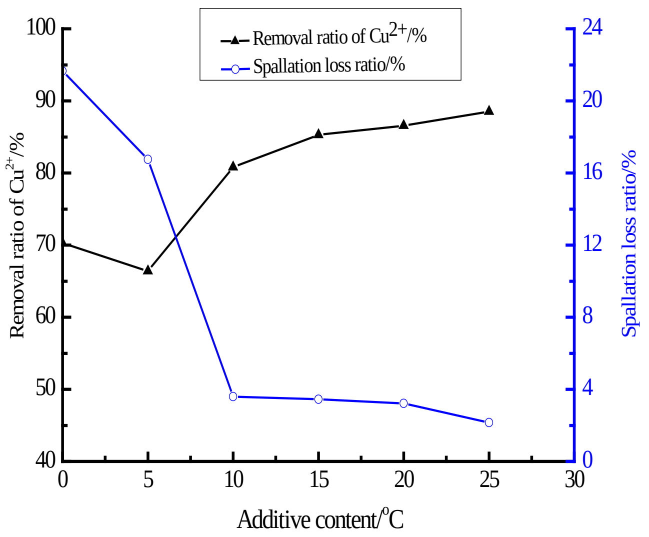

Fig.3 Effect of additive ratio on removal efficiency

Fig.3 showed that adding a few industrial starches could play a role of bonding and decrease granular spallation loss ratio. But bonding effect was unconspicuous and mainly played a role of foaming agent when the additive ratio exceeded 10%. Roasted starch could increase the pore of granular adsorbent with the result that increased the removal rate of adsorption. The additive ratio was determined as 10% of the mixture quality.

D. Effect of Granulated Diameter

A certain quantity of montmorillonite and fly ash were weighed and mixed by the ratio of 6:4. Industrial starch was 10% of the quality of mixture. Granular adsorbents of different diameters were prepared by the technology of 1.3.1 and calcination temperature was 450℃. Adsorption experiment was started after the granules cooled down to room-temperature，and other conditions were as same as 2.1. The results were shown in Fig.4.

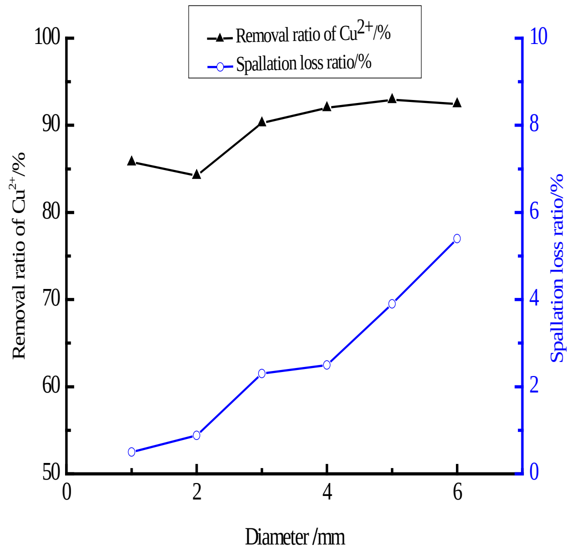

Fig.4 Effect of granulated diameter on removal efficiency

Fig.4 showed that spallation loss ratio and adsorption rate both increased with the increasing of granulated diameter because broken granules increase the surface area. Spallation loss ratio was lower and adsorption rate was higher with smaller granulated diameter. The smaller granulated diameter was，the better adsorption rate. However, there was a problem in practical artificial granulation, so the appropriate granulated diameter was of 1~2mm.

III. ANALYSIS OF PHYSICAL CHARACTERISTICS

The experimental results showed that the optimum technological conditions of preparing composite granules adsorbent materials were as follows: the mixture ratio of montmorillonite and fly ash was 6:4; the calcination temperature was 450℃; the proportion of additive was 10% of the mass of mixture; the diameter of the granular was 1～2mm. Granular adsorption materials of montmorillonite/fly ash were manufactured by the above technological conditions. Water adsorption capacity of granules, apparent porosity and bulk

density were measured by the hydrostatic weighing method. Compressive strength was measured by radial compressing technique and surface area by BET method. The test results are shown in Table 5.

TableV PHYSICAL CHARACTERISTICS OF GRANULATED ADSORPTION MATERIAL OF MONTMORILLONITE AND FLY ASH

Physical property	Test result
Water adsorption capacity (%)	31.80
Apparent porosity (%)	46.82
Bulk density (kg/m^3)	1.47
Compressive strength (MPa)	5.28
Surface area（m^2/g）	10.28

IV. CONCLUSIONS

The above experimental results showed that several factors such as the mixture ratio of montmorillonite and fly ash, the temperature of calcination and the additive proportion had certain influence on intensity and adsorption rate for the granulated composite materials. By comprehensive consideration of the adsorption properties and strength of granules, the optimum technological conditions of preparing the composite granules were determined as follows: the mixture ratio of montmorillonite and fly ash was 6:4; the calcination temperature was 450 ℃; the proportion of industrial starches was 10%; the diameter of the granular was 1～2mm. Using the composite particles prepared by the above technological conditions to treat wastewater containing 200mg/L Cu2+ initially, the adsorption rate could reach 96.34% and the spallation loss ratio was very low. Physical tests and analysis of this materials showed that the water adsorption capacity was 31.80%, the apparent porosity was 46.82%, the bulk density was 1.47 kg/m3, the compressive strength was 5.28 MPa, and the surface area was 10.28m2/g. The composite adsorbent materials prepared under the above conditions exhibited high adsorptive performance.

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